

## New Era will come with New Concept in Refinery

Masaya Kuno

1-7-13 Tsuruma, Machida-shi

Tokyo 194, Japan

Member of JPI

### Keywords:

Conventional crude distillation system to make crude lighter and white oil is theoretically wrong.

### 1) Introduction

Since the "day one", crude had been distilled at first stage, nobody except author has found out the defects of system.

Author had appealed HSP, that is, HydroStripping Process world wide since 1981. This concept was presented in Hydrocarbon Processing September 1981(1), that is, treating crude with hydrogen rich gas for the subsequent vapor phase HDS. Recently, many data have been obtained and found out the following points.

(1) Distillate are not final products, which means it is against 2nd law of energy, that is, increasing entropy of the system.

There exists a possibility in saving energy of the system.

(2) Distillate contain S-Compounds which are able to play the important role in cracking of heavier portion in crude under hydrogen rich gas.

Therefore, distillation operation in first stage is wrong, esp., so when refiner aims to produce white oil and lighter too much.

### 2) What is S-Compound effect ?

S-Compounds in each fraction such Naphtha, Gasoline, Kerocene and Gas Oil must be severely reduced to meet the stringent request of environmental problem. However, such lighter fractions including S-Compounds are dispersed into crude and mixed with heavier portion, which fits the best for heavier portion cracking under hydrogen and hydrogen sulfide at lower temperature without catalyst.

S-Compounds in situ is considered to be a good electron absorber, i.e., hydrogen atom catcher which means hydrogen carrier to cracking portion where S-Compounds promote under hydrogen, radical reaction of heavier portion on the surface of metal. These phenomena is explained from following data.

For example, hydrogen sulfide was used for cracking of polypropylene under hydrogen pressure 3.0 MP at 673 K w/o cat.  $H_2S$  was added to this experiment 1.0vol%, where 97% of distillate product composed of Naphtha 53%, Kerocene 23%, Gas Oil 19% with 2% gas portion were obtained after 1hr on auto-clave test while no addition case showed only 35% distillate and 40% heavier oil and solid state 20% with 5% gas portion. From Journal of JPI Young Society.

This catalytic activity of  $H_2S$  is explained as wall effect of auto-clave metal surface, composed of 18 Cr-8Ni and Fe oxide, which was discovered by Dr. Nakamura, PhD., Fujimoto's room, Tokyo University.

$H_2S$  is so active that it is used as a detective reagent for in-organic Compounds in chemical analysis. This result may be plausible such as sulfiding operation in HDS where  $H_2S$  or  $CS_2$  are used for activation of catalyst surface at start-up.

The importance of this experiment is not only showing the possibility of heavier, asphaltenic and resinic portion reduction but also proposing new phase for theoretical approach of hydrocracking including actual industrial application.

H<sub>2</sub>S may turn to HS<sup>-</sup> + H<sup>+</sup> or so in situ, above 403 K on the transit metals., where proton move so fast following thermal and free electron from wall, or HC that it does not always needs surface area too wide for activation.

Under rising temperature, there begin to exist the unbalanced distribution of electron on HC. H<sup>+</sup> is apt to go to radical portion of HC and HS<sup>-</sup> goes to aromatic portion, where they are cut to be stabilized, that is, each portion become to be the most stable state., which can be judged from the work of Bergius and Pier before World War II. Fig.1, Fig.2

Heavier portion is apt to stick the metal surface due to higher viscosity and unbalanced distribution of electron or so and ready to crack after absorbing thermal electron and hydrogen under acidic environment by H<sub>2</sub>S or so at lower temperature.

The above can be used for explaining about lighter S-Compound effect because they are apt to proceed the metal surface and turn to hydrogen donor or that carbenium ion such HS<sup>-</sup>Compounds after heated up under hydrogen, transferred from in and out cluster on the metal surface, which become radical, hydride rich through protonation (2), while heavier HC is sticky enough to be caught on the metal surface and be enforced to react with them.

H<sub>2</sub>S helps accelerate this transformation such as sulfiding on catalyst where Metal-Sulfur bridge is made on the surface .

H<sup>+</sup> approaches to S-molecule to make H-S compounds or so while HS<sup>-</sup> goes to aromatic compounds on the transit sulfided metal.

Sulfur own effect on coal liquidification reaction is well known, especially, as bronsted acid, under hydrogen at above 703 K. Some process need no catalyst on coal liquefaction except sulfur.

3) Operation condition when treated with hydrogen rich gas.

### 3)-1 Pressure

Too much hydrogen donor is said to stop the radical reaction which also can be explained on the above figures (3).

Hydrogen donor can not transfer electron too much, they cap the cut point and become stabilized by themselves, that is, only become aromatic compounds, which means no need of high pressure hydrogen for hydrocracking of crude. Hydrogen partial pressure is estimated from crude specification, PONA, C/H ratio and metals contents. 2 or 3 MP is enough to keep HS<sup>-</sup> galvanic hydro-sulfide state.

Hydrogen donor is reduced at some rate at Desalter because Fe-Cl compounds have such ability (4). So, Desalter must be installed to reduce Cl, sea water for anti-corrosion and for hydrogen donor.

Radical reaction is also interrupted by cation so that cation should be trapped by anion, esp., Sulfur Compounds .

### 3)-2 Temperature

The reaction temperature is very sensitive because it depends on products spec., to be produced and on its mechanism of reactions. Hydrogenation is exothermic and thermal cracking is endothermic. Where at lower temperature, the former reaction is forwarded while heavier portion is just to be cracked under hydrogen on sulfided metals to naphtha and S Compound by  $H^+$ ,  $HS^-$  and then at higher temperature, the latter reaction is overlapped. Fig. 3

4) The meaning of mixture of heavier oil and lighter oil is as follows.

4)-1 S-Compounds around the heavier cluster become electron, hydrogen deposits when the condition of reaction reach the some level, they will start cracking reaction as catalytic, reactive points.

4)-2 The reactant are transferred through solvent around cluster. But electron rich radical is transferred to heavier unstable portion and continue cracking the remaining heavier portion at above said deposit points.

4)-3 Electronic equivalence of heavier portion seems zero at glance, is very changeable, unstable, depending on around condition so that even slight lighter portion can make better reaction condition to crack such as solvent effect which disperse heavier portion wider and make it differential parts to separate electronically and help radical approach to right points.

4)-4 Too much condensed state such carbonaceous asphaltene, resin and metals complex should be avoided because they are promoting their familiar components production when making white oil, even burning oil to meet such as CAAA in U.S.A..

4)-5 Recently, soluble metal compounds have been informed to exert much more catalytic activity in coal liquefaction (5).

Therefore, without catalyst, more preferable reactive field may be obtained in lighter crude oil which contents metal compounds.

Because only catalyst is solid and interrupt mixing effect, transfer of heat and etc. while hydrogen partial pressure, sulfur compounds, transit metal's surface and temperature are indispensable factors.

### 5) Conclusion

From thermodynamic, chemical reactionary and electrical equivalent points of view, existing atmospheric distillation is of problem, not economical when refiner need white oil and light oil too much.

Conventional refinery system is of try and error concerned technology, experimental technique. However, recent developed technology has begun to reveal the intrinsic quality of such intricate complex compounds.

Tubes of heat exchangers and pipe lines have enough surface to be activated by  $H_2S$  and S-Compounds with hydrogen, on alloy steel.

This new concept, treating crude with hydrogen rich gas leads to Bottomless Refinery, Jet Fuel and Naphtha Rich Refinery, therefore, Refiner should treat the crude under hydrogen at first stage if refiner want to obtain lighter and white oil too much at the lowest cost.

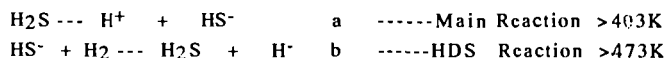
Under hydrogen treating and HDS combination, thiophene is not produced. Heavier residue Catalytic Cracking Process is not to be used any more, the same as sweating process of lighter HC.

Ironically, S-Compounds are indispensable for hydrocracking, not suitable for burning hydrocarbon, which leads us to contemplate that that mysterious, historical birth of the Earth. We are now struggling against environmental problem evoked by noble petroleum, sulfur and oxygen, aiming at sustainable economic development.

Reference only,

$\text{HS}^-$  may become  $\text{H}_2\text{S}$  at high press  $\text{H}_2$ . There needs some state to be maintained for reaction field where  $\text{HS}^-$  may continue to decompose the heavier hydrocarbon like sharp knife edge with  $\text{H}^+$  and electron.

Typical reaction are as follows.



a + b



These basically reaction are proceeded through or on the S-M bridge. Each equation depends mainly on temperature and hydrogen pressure. Equation c is rarely occurred and has not detected so far.

Literature cited.

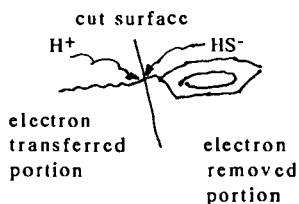
- (1) Masaya Kuno, Hydrocarbon Processing (1981)
- (2) B.W.Wojciechowski, Symposium on Hydrogen Transfer in Hydrocarbon Processing ,ACS (1994)
- (3) Junich Kubo H. Higashi, Y Ohmoto and H Arao ditto.
- (4) John H. Penn and Jinhai Wang ditto.
- (5) T. Kondoh, A. Matsumura, K. Okegawa, I Saitoh, Sigen and Kankyo Vo.2, No.5 (1993)

Reference

Dr. Kabe, 1983, treated Taching Crude with hydrogen,  $\text{CS}_2$  as activator, toluene as solvent and catalyst Ni-Co-Al Oat 673 K. under hydrogen pressure 100 K/G, reaction time 5 hr using autoclave. No activator case showed nothing particular.

The result was residue 40% down, while Naphtha increased 5 times that is, 30 wt% and middle increased a little, 20 to 25 wt%.  
Journal of JPI, Vol 26 No3 1983.

Fig.1 shows the typical image



sulfided composition is stabilized

lighter S Compound is made.

lighter portion  
is produced  
heavier

where is cut is depends on the  
solvent spec, around the

(Hexane soluble) { Benzene } HC and on other condition such  
(and the like) { soluble or so } temp or so.

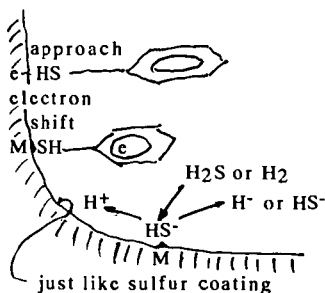
Heat of hydrogenation is enough to cut c-c bond at above 573K.

Produced heat of hydrogenation is transferred around lighter solvent and / or activate another portion to be radical.

Fig.2 shows the typical image on metal surface

on the surface of metal

Thermal electron comes from  
heated metal surface through  
Metal-Sulfur bridge



Electron proceed and move to  
aromatic Compounds which is  
under lower electron density.

When electron become rich in  
aromatic Compounds.  $H^+$  can  
easily approach and cut the  
 $C=C$  bonds after hydrogenation.

M-S bridge also protect to transfer thermal electron from  $C=C$  bonds hydrocracking to metal surface, which cause not to evoke carbon making.

Fig. 3 shows the operational condition

